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(54) Mineral filled seals for galvanic cells

(57) Mineral filled polypropylene (as a preferred embodiment), but also filled thermoplastic material that is inert to electrolyte, such as polypropylene, polyethylene, copolymers thereof, and nylons is used for injection molded seals comprising rupturable vent members for galvanic cells. The mineral is generally talc. (anhydrous magnesium silicate) but may be calcium carbonate or mica, or oter electrolyte-inert material.

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SPECIFICATION

Mineral filled seals for galvanic cells

This invention relates to sealed galvanic cells, such as primary alkaline cells and the like, and particularly relates to sealing and insulating members, hereafter referred to as seals, for such cells; which are produced or molded from filled thermoplastic material such as polypropylene, filled with a mineral, particularly talc, calcium carbonate or mica.

The general construction of a sealed, cylindrical galvanic cell is such that its principal components, an anode and a cathode, are assembled into a can, together with the appropriate separators, electrolyte, etc., and the cell is then closed by a seal placed in the open end of the can. The seal precludes electrolye leakage from the cell and insulates the electrode contacts of the cell from each other.

A seal will desirably also permit hydrogen gas permeation from the cell so as to reduce pressure build-up within the cell, and yet also to inhibit moisture gain or loss, and oxygen or carbon dioxide infiltration into the cell. Still further, the seal is usually manufactured with a molded-in membrane or thin section so as to assure that the cell will vent under certain conditions when high gas pressure buildup within the cell may occur, and to preclude rupture of the cell.

In keeping with the present invention, seals are provided for use in cylindrical sealed cells and are molded, generally injection molded, from a filled electrolyte inert thermoplastic material, such as polypropylene, polyethylene, and nylon, (and particularly for high temperature applications, polysulfone), and co-polymers thereof; usually polypropylene having from 5% to 45% by weight of mineral filler, where the mineral may be chosen from the group consisting of talc [theoretically anhydrous magnesium silicate, $Mg3SiO10(OH)2$], calcium carbonate, and mica. Depending on the purpose for which the seal may be used, it may be annealed or not. When polypropylene is annealed, it may be annealed at temperatures of 70 degrees C to 155 degrees Celcius, (other temperatures being appropriate for other thermoplastic materials such as co-polymers or polypropylene, polyethylene and nylon). Desirably the annealing can be performed in an air-circulating oven or tunnel. In most instances, mineral filled polypropylene, and particularly talc filled polypropylene, has been found to be particularly useful.

As noted above, any seal made according to this invention, such as a filled may be provided having a rupturable membrane vent area that has a reduced cross-sectional thickness relative to the thickness of the material surrounding the membrane. The precise configuration of the rupturable membrane vent area is not specifically a subject of the present invention, and the sealing and insulating member may take the kind of appearance as those that are described in the co-pending British patent Applications 82,36556 and 8318257 all of the aforementioned co-pending Applications being assigned to a common Assignee herewith. The seal may otherwise be of any other suitable design.

A number of advantages are realized by using filled thermoplastic for molding sealing and insulating members. The advantages that are achieved include molding and manufacturing economies with a better product, mechanical advantages as to the assembly of the cell and design tolerances, chemical advantages as to the presence of the member in the cell, and physical advantages that give rise to enhanced cell operation and assist in the mechanical and molding advantages.

For example, injection molded plastic parts that are made from talc loaded polypropylene can be produced substantially without any sink marks; i.e., surface cavitation or irregularities, which may be particularly important when the seals are formed having a membrane. Moreover, because the parts can be molded without sink marks, the molding tolerances and conditions under which the parts are molded are less critical.

A mineral filler, such as talc, can permit lower molding temperatures. Also, a minerall filler such as talc may add lubricity to the surface of the thermoplastic material, so that it can act as an internal mold release agent. This is particularly helpful because external mold release agents such as silicones may contaminate the molded parts, and that contamination in turn can cause gassing with in the cell. The mineral filler (talc, calcium carbonate or mica) would not cause gassing within the cell. Because there is less shrinkage after molding, especially with higher concentrations of filler such as talc in the 20% to 40% range, there is greater assurance that the sealing and insulating members will be more precisely molded. Finally, the cost per piece of mineral filled plastics may be less than that of unfilled materials.

We have discovered that there are substantial mechanical advantages that are gained through the use of filled thermoplastic material. These include the fact that there are better sealing and venting characteristics of the member. A filled thermoplastic has lower co-efficient of linear thermal expansion, which relates more closely to the co-efficient of linear thermal expansion of the metal can that is used for assembly of the cell. This results in a better seal, particularly following thermal cycling. The filled thermoplastic has a higher compressive strength than an unfilled material, resulting in a better seal at the crimp. That feature is even more greatly enhanced when the sealing and insulating members are

annealed. The annealing stabilizes the dimensions of the sealing and insulating members; that is, the physical dimensions of the part becomes constant, and annealing also relieves any molded-in stresses that may have been caused during the molding process.

The filler acts as a stress concentrator to allow for the venting or membrane rupture to occur at minimal membrane deflection. When a filled seal is annealed, thus relieving any molded-in stresses that may have occurred, the membrane rupture pressure increases relatively less than the corresponding increase imparted by annealing an unfilled material. An annealed filled material provides greater predictability of the rupture strength of a membrane.

At the same time, the provision of a filled thermoplastic reduces the headroom requirements by assuring that the rupturable vent will rupture with less stretching than an unfilled thermoplastic material, and without excessive pressure build-up in the cell. Moreover, a thicker membrane may be molded, thereby permitting wider molding tolerances, while still remaining within the venting tolerance design.

Also, because there is less headroom needed to permit vent rupturing, the seal may be placed slightly higher in the can, thus permitting installation of a greater amount of active material in the cell.

We have also discovered that lower molding temperatures may be possible. At the same time, when the filled thermoplastic is injection molded, its cooling characteristic in the mold is sufficiently better than that of an unfilled material that the molding cycle may be reduced while at the same time broadening the "window" of the instant of time during the molding cycle when a pin must be moved in the mold to accommodate the molding of the thin membrane section.

Because the filled thermoplastics of the invention permit hydrogen permeation, the cell in which the member is installed may trickle vent. Trickle venting permits sufficient hydrogen to escape from a cell, thus reducing the possibility of venting of the cell by membrane rupture. This is also important in that the amount of mercury corrosion and gassing inhibitor constituent that may have to be installed in the cell, particularly in alkaline cells, may be reduced quite considerably, thereby resulting not only in a more environmentally satisfactory product, but also in better working conditions for assembly of the cell, and appreciable cost savings.

An advantage that arises from the present invention when compared to glass filled nylon, when used for cell seals, is that the filled thermoplastic is much less subject to leaching when it is exposed to electrolyte such as 40% potassium hydroxide solution. That is, talc, calcium carbonate or mica filled polypropylene will not decompose, even when exposed for long periods of time say four weeks at 71°C to KOH, such as the glass filled nylon does.

The filled thermoplastic materials that are considered herein, such as talc, calcium carbonate or mica filler, in quantities of from 5% to 45% and usually 15% to 40%, the filler material is very finely ground or is a fine particulate material; and is such that when it is within the molded thermoplastic sealing and insulating member, there is substantially no surface exposure of the filler material in the molded part. In that regard, particularly with respect to the use of talc as a filler, it is preferred that approximately 20%, but up to 40% talc, may be used as a filler, particularly in polypropylene.

As noted, annealing provides certain advantages by relieving any molded-in stresses that may have occurred, and stabilizing the physical dimensions of the molded sealing and insulating member; but even if the seal is unannealed, superior performance over an unfilled product of similar design can be achieved. This is because there is a wider tolerance in the production of the membrane portion of the member, so that it can be molded thicker, with better prediction as to the rupture pressure, and in any event so as to accommodate somewhat higher rupture pressures without approaching the pressure at which the cathode can would decrimp causing release of the whole member and thus rupture of the cell.

A typical analysis of talc-filled polypropylene follows:

The polypropylene resin, unfilled, may have a melt index of 10 to 15. After filling, the melt index will have been reduced to about 6 to 10.

The talc is a platy or platelet-like dusty white powder substance, having no asbestos constituent, and having a chemical analysis that may be within the following ranges:

CONSTITUENT	% BY WEIGHT
MgO	20–32%
SiO_2	16.46%
CaO	9–30%
Al_2O_3	0.5–4%
Fe_2O_3	0.2–4%
LOI	8–20%

[LOI (Loss on Ignition) represents the percentage of carbon dioxide released on heating of the talc.]

A typical mesh-size distribution of Particle size may be within the following ranges:

MESH SIZE PASSED	% BY WEIGHT
44 microns	100%
30 microns	94–97%
20 microns	75–90%
10 microns	40–60%
5 microns	18–32%
4 microns	14–24%
3 microns	9–17%
2 microns	5–10%
1 micron	4–4%

Typical dry brightness is 84–94; tapped density is 60–80 lbs/cu.ft.; loose density is 24–55 lbs./cu.ft.; specific gravity is 2.8–2.9; oil absorption g/100 g talc is 20–35; pH is 9–10.5; Hegman fineness is 1–3.5; 100% will pass 200 mesh and 98–99.9% will pass 325 mesh.

A similar ground calcite (calcium carbonate) would exhibit the following characteristics:

CONSTITUENT	% BY WEIGHT
$CaCO_3$	95–98%
$MgCO_3$	1–2%
Al_2O_3	0.05–0.2%
Fe_2O_3	0.01–0.2%
SiO_2	0.1–1%
MnO	.01%
Copper	not detected
Moisture	0.25%
Organic Coating (typically silane)	0.5–2%

Typical particle size is 100% less than 15 microns (spherical particles); with 95–99% less than 10 microns; 75–85% less than 5 microns; 40–60% less than 2.5 microns; and 20–40% less than 1 micron. The mean particle size may be in the order of 2.5 microns; with a specific gravity of about 2.7 and a refractive index of approximately 1.55.

Several examples follow:

EXAMPLE 1:

A number of AA sized seals (tops) were molded from nylon, unfilled polypropylene, and polypropylene having 20% talc filler. Half of each of the polypropylene tops were annealed, and the other half were not. All of the tops were fully installed in cells, except that the outer jacket was not placed on the cell, and observations of leakage were taken following various storage and use tests.

Leakage observations revealed, for example, that after storage for one week at high temperature, and a further week of room temperature stabilization, the annealed tops and the ... thirty) and no failure, with higher failure of the unanealed tops. Other tops were stored at a somewhat lower, but still elevated temperature, for two weeks, followed by a further week of room temperature stabilization, with one nylon and one unfilled top failing, while no filled top failed.

Still other tops underwent storage at very low temperature for one week, followed by room temperature stabilization for another week, with much better performance for annealed filled tops (one of thirty) for example, than the nylon tops of which 20 of 30 failed.

Likewise, temperature cycling of another batch from low temperature to a relatively high temperature followed by room temperature stabilization showed failure of only two of thirty annealed filled tops, while 15 of the thirty nylon tops failed.

Other samples were stored at room temperature for one day, after which they were subjected to a 1.5 ampere charge, and all cells vented. However, other tops were stored at high temperature for several days and then given a 1.5 ampere charge; and three of three filled annealed polypropylene tops vented, whereas one of three of the cells having a nylon top had a much more violent rupture.

EXAMPLE 2:

A number of AA, C and D cell tops were molded, all having rupturable vent membranes molded in them having thicknesses of from 0.0035 to 0.005 inch; and of the molded samples, some were molded without talc filler, some had 20% talc filler and some had 40% talc filler.

A number of tops were chosen as controls, and were not immersed in potassium hydroxide solution; whereas other groups of tops were immersed in potassium hydroxide solution at room temperature for two weeks, or a high temperature for two weeks, or a very high temperature for two weeks. Thereafter, out-of-cell vent testing was performed, by which all of the tops that had been stored while immersed in KOH showed venting results that were quite consistent with the control group that had not been exposed to or immersed in KOH. In other words, all of the samples were chemically resistant to the KOH solution.

An important conclusion that can be drawn from these venting tests is that the membrane or vent pressure relief portions of the filled polypropylene tops are not affected by alkaline electrolyte at high temperature; and that the membranes will rupture so that the cells will vent at the same pressure both before and after long storage at elevated temperatures. The same conclusion can be drawn with respect to the other filled thermoplastic materials discussed herein.

Other venting tests were carried out, wherein tops having vent membranes of a thickness of 0.0055 inch molded therein were tested in the presence of various height clearances above the membrane. Unfilled polypropylene tops failed to vent or vented at very high pressures with low clearances, whereas 20% talc filled tops vented at reasonable pressures. At 0.091 inch clearance, an unfilled and unannealed polypropylene top did not vent at a pressure of 850 psi; whereas a similar top having 0.145 inch clearance vented at 280 psi. Unannealed 20% talc filled polypropylene tops vented at 480 psi with the lowest clearance noted above, and at 280 psi with the highest clearance; whereas annealed 20% talc filled polypropylene tops vented at 420 psi with the lowest clearance and 400 psi with the highest clearance.

EXAMPLE 4:

Glass filled nylon, unfilled polypropylene, 20% talc filled polypropylene and 40% talc filled polypropylene tops were molded, after which they were stored at 71°C for one month in KOH electrolyte. The solution following the storage was acidified and analyzed for traces of metallic elements. Except for a slightly higher reading of calcium leached from the 20% talc filled polypropylene tops, none of the polypropylene tops showed any significant leaching of nickel, cadmium, strontium, cobalt, titanium, molybdenum, lead, copper, iron, vanadium, chromium, aluminum, silicon or calcium. The glass filled nylon, on the other hand, showed that significant amounts of titanium, copper, iron, vanadium, aluminum, silicon and calcium had been leached.

The use of filled thermoplastic materials, notably but not exclusively mineral filled polypropylene, and particularly talc filled polypropylene, as a material for injection molding of seals or tops for cells has been discussed above. In some respects, the action of filled and unfilled polypropylene have been observed to be substantially the same; whereas in other respects, the action of materials such as filled polypropylene (with 20% to 40% of talc in the tests specifically referred to) have shown marked improvement over unfilled polypropylene, and over such other materials as glass filled nylon. That improvement has been particularly noted in respect of predictable venting pressure and venting operation by rupture of the membrane, and an ability to withstand temperature cycling.

Moreover, considerable other advantages are obtained by filled polypropylene when compared to unfilled polypropylene, including better molding characteristics at lower molding temperatures, better sealing characteristics; and permitting wider design and molding tolerances.

In all events, the filled polypropylene tops that were specifically tested also showed better results than commercial nylon or glass filled nylon tops.

The configuration of filled thermoplastic seals according to the present invention is dependent upond esign considerations that are beyond the scope hereof; but the designer may permit wider tolerances in molding, and he may design for thicker rupturable vent membranes with the assurance that cell performance will be as expected when the cells are in the field.

The appended claims, however, define the ambit of the present invention, as herein set forth.

CLAIMS

1. For use in crimp sealed galvanic cells, a seal composed of a thermoplastic material having from 5% to 45% by weight of filler, wherein said thermoplastic material and said filler are each chemically inert to the electrolyte material that will be used in the sealed cell, and having a rupturable member vent area with reduced cross-sectional thickness relative to the thickness of the material surrounding said vent area.
2. The seal of claim 1, in which said thermoplastic material is chosen from polypropylene, polyethylene, and co-polymers thereof; and said filler is chosen from talc, calcium carbonate, and mica.
3. The seal of claim 2, when made from polypropylene having talc filler.
4. The seal of claim 3, when talc is present in the amount of 15% to 40%.
5. The seal of claim 4, wherein said talc has a particle size less than 44 microns maximum dimension, with at least 2% by weight greater than 1 micron, at least 18% greater than 5 microns and at least 40% greater than 10 microns.
6. The seal of any preceding claim, when annealed.
7. The seal of claim 4 or 5, when annealed at a temperature from 70°C to 150°C.
8. The seal of claim 4 or 5, when annealed for at least 1 hour at a temperature of from 70°C to 155°C.
9. A seal for crimp-sealed galvanic cells, as claimed in claim 1 and substantially as herein described.
10. A galvanic cell comprising a container crimp sealed with the seal of any of claims 1 to 9.

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